Journal of Physics and Chemistry of Solids 121 (2018) 276–284

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Electronic structure, stability, and magnetism of rutile-type ultrathin TiO_2 nanotubes

Yongjia Zhang*, Ninggui Ma, Min Zhou, Ensi Cao**, Li Sun, Wentao Hao, Zhi Yang

Key Lab. of Advanced Transducers & Intelligent Control System, Ministry of Education, College of Physics & Optoelectronics, Taiyuan University of Technology, Taiyuan, 030024, People's Republic of China

ARTICLE INFO

Keywords:
Ab initio calculation
Ferromagnetism
Intrinsic defect
TiO_2 nanotube

ABSTRACT

In this study, based on density functional theory, we predicted the electronic structure, stability, and magnetism of ultrathin rutile-type TiO_2 nanotubes (u-TiO_2NTs) with different curvatures. The curvature energy calculations showed that the (m, 0) u-TiO_2NTs follow the classical elasticity theory. As the diameter of the NTs increases, the wall thickness becomes thinner, and the binding energy and band gap increase until saturation. For the (10, 0) u-TiO_2NT, the neutral Ti vacancies (V_{Ti}^0) could induce a large magnetic moment and long-range ferromagnetic coupling, whereas the neutral O vacancies (V_O^0) cannot. In addition to calculations of the vacancy formation energy, we investigated the magnetism and magnetic coupling of the (10, 0) u-TiO_2NT with V_{Ti}^- or V_O^+. We found that the introduction of V_{Ti}^- vacancies led to unstable ferromagnetic coupling in the NTs, whereas the V_O^+ vacancies preferred to couple in a stable ferromagnetic manner. Our results suggest a possible route for obtaining high Curie temperature ferromagnetism in TiO_2 materials.

1. Introduction

Titanium dioxide has been investigated extensively in the past two decades because of its fascinating electronic, catalytic, optical, and magnetic properties [1–4]. In addition, due to its low cost synthesis, environmental stability, and non-toxicity, TiO_2 can be used widely in many fields, such as gas sensing, solar-to-chemical energy conversion, environmental cleaning (photodecomposition of harmful materials and dirt), and spintronic devices [4–7]. Since the first discovery of room-temperature ferromagnetism (RTFM) in a Co-doped TiO_2 thin film [3], numerous studies have focused on magnetism in metal- or nonmetal-doped TiO_2 [8–11]. Several models have been proposed to explain the origin of magnetism in doped TiO_2, such as the charge transfer model [12], Stoner-type model [13], and band coupling model [14].

In recent years, many studies have confirmed the detection of room-temperature spontaneous magnetization in undoped TiO_2, which is known as d^0 magnetism. Some experimental findings have shown that the saturation magnetic moments of TiO_2 thin films decrease as the annealing time increases in an oxygen atmosphere and that vacuum annealing enhances the RTFM, thereby indicating that the RTFM is closely related to the O vacancy instead of the Ti vacancy [15–17]. Results obtained based on density functional theory (DFT) indicate that the ferromagnetism in TiO_2 nanocrystal could possibly be ascribed to the holes introduced by the Ti vacancies [18]. In addition, studies suggest that the Ti vacancy can cause a high-spin defect state and ferromagnetic coupling, whereas the oxygen vacancy reduces two Ti^{4+} ions into Ti^{3+} to yield a stable antiferromagnetic state [19]. More recently, a new mechanism has been proposed for multi-defect induced ferromagnetism, where the Ti vacancy produces the local magnetic moments and the electrons induced by the O vacancy mediate long-range ferromagnetic coupling [20].

Most previous studies of ferromagnetism have focused on TiO_2 thin films and bulk crystals, whereas few have investigated the magnetic properties of TiO_2 nanotubes (NTs) [21,22]. Due to the rapid development of experimental techniques, TiO_2 NTs have been fabricated successfully using various methods, and their properties have been studied extensively, including the photocatalytic activity, electrochemistry, adsorption, and structural stability [23–26]. It has been shown that intrinsic defects in the lattice are unavoidable under different growth conditions, which can introduce local magnetic moments [15–20]. Compared with thin films and nanocrystals, one-dimensional NTs with a high surface area can make it easier to obtain many useful vacancies. In our previous study, we investigated the electronic and magnetic properties of oxygen- and titanium-deficient anatase-type TiO_2 NTs, respectively. We found that the Ti vacancies could introduce a large magnetic moment and stable ferromagnetic coupling, whereas

---

* Corresponding author.
** Corresponding author.
E-mail addresses: zhangyongjia@tyut.edu.cn (Y. Zhang), caoensi@163.com (E. Cao).

https://doi.org/10.1016/j.jpcs.2018.05.038
Received 3 January 2018; Received in revised form 24 May 2018; Accepted 25 May 2018

the magnetic coupling types induced by oxygen vacancies were related to the types of vacancies [27]. In addition, recent experimental results have shown that the magnetic property of undoped TiO_2 NTs is sensitive to the tubular structure, and the measured magnetic moment of rutile-type TiO_2 NTs is smaller than that of anatase-type NTs [28]. Moreover, it has been shown that the bridging O vacancies can induce magnetic moments in oxygen-deficient rutile TiO_2 (110) surfaces [29] and this finding has been extended to other low-index rutile TiO_2 surfaces, such as (100), (101), and (001) surfaces [30]. Many studies have investigated the magnetism induced by point defects in rutile TiO_2 surfaces, but few have discussed the electronic structure and magnetic properties of rutile-type TiO_2 NTs. Thus, in this study, we systematically determined the electronic structures and magnetic properties of the rutile-type ultrathin TiO_2 NT (u-TiO_2NT) with various intrinsic defects, and the magnetic coupling mechanism was also investigated.

2. Computational methods

Our calculations were performed by applying the pseudopotential method based on DFT in the local density approximation (LDA) scheme using the spin-polarized mode, where we employed the Vienna ab initio simulation package (VASP) using the projector augmented-wave method [31]. In order to correct the underestimated band gap, we used the LDA + U method to treat the partly occupied 3d orbitals of Ti [32]. In our calculations, the on-site effective parameter, U_{eff} ($= U - J$), was set as 5.8 eV, which has been shown to yield reliable results in terms of the electronic and atomic structure of the TiO_2 bulk crystal [19,20]. u-TiO_2NT can be formed by rolling up one rutile TiO_2 nanosheet along a certain crystallographic axis. Moreover, the periodic boundary condition along the tube axis was employed for the NT with a vacuum region (10 Å) between tubes in order to ensure that there was no interaction between them. An energy cutoff of 450 eV was used for the plane-wave expansion of the electronic wave function. The special k point was generated with a $1 \times 3 \times 1$ grid based on the Monkhorst–Pack scheme. To obtain the equilibrium structure, we allowed the lattice constants and all atoms in the NT to relax. Good convergence was obtained with these parameters. The total energy converged to 1.0×10^{-4} eV/atom in the optimized structure.

3. Results and discussion

3.1. Structural properties, stability, and magnetism of pristine u-TiO₂NT

A key reason for selecting rutile-type TiO_2NTs is that rutile TiO_2 has the most stable thermodynamic structure in three basic crystalline phases (rutile, anatase, and brookite) [33]. Clearly, an isolated nanosheet is the starting point for the tubular forms, such as graphene for carbon NTs. In the framework considered in the current study, the nanosheet is cleaved from the relaxed rutile TiO_2 supercell and it comprises two TiO_2 planes, as shown in Fig. 1(a). Fig. 1(b) shows the structure of the TiO_2 nanosheet after relaxation. The Ti-O bond lengths are reduced in the optimized model compared with the pre-optimized model, and the two original TiO_2 planes are transformed into three alternating Ti and O atoms layers. The rolling up direction for u-TiO_2NT is represented by the chiral vector: $\boldsymbol{C}_v = m\boldsymbol{a}_1 + n\boldsymbol{a}_2 \equiv (m, n)$, where $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ denote the primitive translation vectors of the lattice, as shown in Fig. 1(b). In the present study, we investigated (m, 0) u-TiO_2NT, as shown in Fig. 1(c) and (d). For (m, 0) u-TiO_2NT, the O and Ti atoms form a three-layer concentric cylinder, where the O atoms are located on the inner and outer cylindrical layers, whereas the Ti atoms reside on the middle cylindrical layer. The tube diameter D is determined by the number of TiO_2 unit cells m arranged in the circumferential direction, where D is estimated by taking the average of the inner and outer diameters: $D = (D_{\mathrm{out}} + D_{\mathrm{in}})/2$. D_{out} and D_{in} are labeled in Fig. 1(c). In order to systematically study the properties of u-TiO_2NT, we simulated NTs with different values of D (m is from 4 to 15). It should be noted that a tubular model cannot be constructed if the value of m is 1 or 2. In addition, when the value of m is 3, the tubular structure will be broken after optimization. Thus, in our simulations, the smallest allowable size used for u-TiO_2NT was $m = 4$. Given the importance of Ti-O bonds during the formation of the NTs by bending nanosheets, we calculated the Ti-O bond lengths in the NTs with different diameters D and the results are presented in Table 1. Clearly, as the tube diameter D increases, the bond length of Ti-O$_{\mathrm{in}}$ increases and that of Ti-O$_{\mathrm{out}}$ decreases (O$_{\mathrm{in}}$ and O$_{\mathrm{out}}$ are labeled in Fig. 1(c)). This demonstrates that the tension in the outer layer and the pressure in the inner layer are reduced, which implies that the structure of the NT tends to be stable. In addition to the Ti-O bond length, we considered the wall thickness ($\Delta\Phi$) of the NTs. Fig. 2(a) illustrates the dependence of $\Delta\Phi$ on the diameter D of the NTs with different m values, where $\Delta\Phi$ was calculated by taking the difference between the radii of the outer and inner layers (see the inset in Fig. 2(a)). The results show that the value of $\Delta\Phi$ decreases for the NTs as the diameter D increases. In addition, the variations in $\Delta\Phi$ in the fitted data decrease greatly from (10, 0) u-TiO_2NT, thereby indicating that the forces become more balanced on both sides of the tube wall.

To verify the stabilities of the nanosheet and u-TiO_2NTs, we investigated their binding energies per atom, which can be defined as [34]:

$$E_{BE} = -[E(TiO_2\ system) - xE(Ti) - 2xE(O)]/3x, \tag{1}$$

where E(TiO_2 system), E(Ti), and E(O) are the total energy of the TiO_2 system (nanosheet or NTs), the atomic energy of an isolated Ti, and that of an isolated O, respectively. As shown in Fig. 2(b), E_{BE} is 7.12 eV in the pre-optimized TiO_2 nanosheet and 7.88 eV for the optimized TiO_2 nanosheet, which indicates that the optimized model is more stable. For the u-TiO_2NTs with different values of m, E_{BE} increases as the tube diameter D increases and approaches a saturation value. The formation of the tubular structure changes the Ti-O bond length slightly due to the curvature effect. The Ti-O bands are elongated in the outer cylindrical layer whereas they are shortened in the inner cylindrical layer. The bond lengths of Ti-O$_{\mathrm{in}}$ and Ti-O$_{\mathrm{out}}$ in the NT tend to be equal as the tube diameter D increases, thereby demonstrating that the stability of u-TiO_2NT is related to the structural symmetry of the tube wall. In addition, E_{BE} is much smaller for u-TiO_2NT than the optimized TiO_2 nanosheet, which suggests that the tubular structure of TiO_2 is not as stable as the two-dimensional nanosheet, mainly because the structures of the two sides of the TiO_2 nanosheet are highly symmetrical. Similar results were obtained for ultrathin ZnTe, SiC, and CdS NTs [32,34,35], but not for ultrathin $PbTiO_3$ NTs [36]. This difference is due to the structural asymmetry on both sides of the $PbTiO_3$ nanosheet, which leads to the spontaneous curling of the nanosheet. The curvature energy is another important quantity when assessing the structural properties and stability of u-TiO_2NTs, where this parameter reflects the mechanical tension in u-TiO_2NTs and it can be defined as the energy needed to form a NT from a two-dimensional nanosheet. The curvature energy of each atom in the NTs is calculated by taking the difference between the binding energies per atom in the nanosheet and NT. Thus, the curvature energy per atom can be expressed as [34]:

$$E_c = E_{BE}(TiO_2\ nanosheet) - E_{BE}(TiO_2\ NT), \tag{2}$$

where E_{BE}(TiO_2 nanosheet) is the binding energy of each atom in the two-dimensional nanosheet and E_{BE}(TiO_2 NT) represents the binding energy per atom of an u-TiO_2NT constructed from the same nanosheet. We calculated E_{c} for u-TiO_2NTs with different diameters D, and the variations in E_{c} with respect to $1/D^2$ for all of the NTs are shown in Fig. 3(a). Clearly, E_{c} in the u-TiO_2NT is approximately proportional to the inverse square of the tube diameter D. The variations in E_{c} as a function of the tube diameter D can be fitted to the data using the expression: $E_{\mathrm{c}} = E_{\mathrm{o}} + \alpha/D^2$, where E_{o} corresponds to the curvature energy of the TiO_2 nanosheet. According to the best-fitted line, E_{o} and α were calculated as 1.66 eV and 5.75 eV/Å, respectively, which suggests that the structures of the u-TiO_2NTs follow the law of classical elasticity.